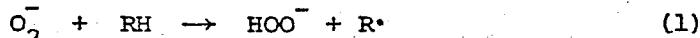


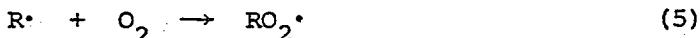
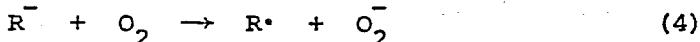
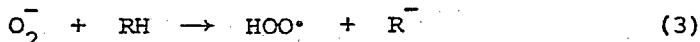
Superoxide Mediated Oxidation of Hydrocarbons in Aprotic Media -
The Question of Mechanism

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A good deal of research has been carried out on the O_2^- induced oxidation of hydrocarbons.¹ Lee-Ruff and Timms² have recently reported that O_2^- mediated autoxidation of fluorene and diphenylmethane proceeds via an initial benzylic hydrogen abstraction by superoxide (equation 1 and 2). Simple thermochemical



calculations, however, cast serious doubt on the role of superoxide as a hydrogen abstractor, except perhaps with exceptionally labile hydrogens. Alternatively, in light of superoxide's impressive effective basicity, a mechanism involving O_2^- induced base catalyzed autoxidation (equations 3-5) is



more likely. Indeed a Hammett ρ plot for the reaction of O_2^- with various substituted diphenylmethanes gives a ρ value of >4 . This confirms the suggestion that deprotonation (equation 3), not hydrogen atom abstraction (equation 1) is the rate determining step.

References

- 1a. A. A. Frimer in "The Chemistry of Functional Groups: Peroxides," S. Patai, ed., Wiley-Interscience, New York, 1982, pp. 429-461.
- 1b. A. A. Frimer in "Superoxide Dismutase," Vol. II, L. W. Oberley, ed., Chemical Rubber Co: Boca Raton, Florida, 1982 (in press).
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A NOVEL HUMAN COPPER-CONTAINING SUPEROXIDE DISMUTASE.

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A novel superoxide dismutase was isolated from human lung. It has a molecular weight around 135000 and is composed of four equal non-covalently bound subunits. It possesses four copper atoms and has hydrophobic properties. It is a glycoprotein. It has a high activity, $4.5 \times 10^9 M^{-1} s^{-1}$. The distribution in tissues and extracellular fluids will be presented.